The nickel-chlorine bond distance in $Ni(dtco)_2Cl_2$ is shorter than in other octahedral nickel complexes containing axial chlorine atoms by 0.03-0.16 Å,[17-19] probably due to the weak bonding of the thioether donor.

The nickel-thioether sulfur distance in the binuclear square-planar complex Ni_2[bis(2-mercaptoethyl) sulfide]$_2$[20] is much shorter (by 0.34 Å) than the nickel-sulfur distances in $Ni(dtco)_2Cl_2$, due not only to the smaller number of bonds to the nickel atom but also to the thioether donor being held closely to the nickel atom by ligand strain. The nickel-sulfur distances in $Ni_2(dtco)_2Cl_2$ are much longer (by about 0.33 Å) than in square-planar complexes containing saturated thiolate complexes[20,21] and are about the same length as in thioketone complexes (2.46 Å[18] and 2.51 Å[22]). There appears to be close contact, and therefore repulsion, between the chlorine atom and ligand hydrogen atoms in $Ni(dtco)_2Cl_2$ which probably results in longer nickel-sulfur distances than would be expected in thioether complexes which lack similar repulsions.

The sulfur-carbon distances in $Ni(dtco)_2Cl_2$ (1.81 Å) are typical of single S-C bonds found in sulfur-containing transition metal complexes (1.80-1.87 Å[20,21,23,24]) and in uncomplexed dithiane (1.80, 1.82 Å[25]).

S-C-C (115-124°) and C-S-C (102, 103°) angles are close to those measured in other thioether complexes[23,24] and in dithiane[25] (108-117° for S-C-C and 95-102° for C-S-C). The measured C-C-C angles are much larger than the tetrahedral angle, most of this effect presumably being caused by the disorder described above. Some ligand strain may also be involved: the C-C-C angles in 1,5-diazacyclooctane-*N,N'*-diacetatoaquonickel(II) dihydrate are about 116°.[6]

X-Ray powder diffraction spectra show that $Ni(dtco)_2Cl_2$ is not isomorphous with any nickel(II) or copper(II) complexes studied to date.[5] However, $Ni(dtco)_2I_2$ may have a similar structure, since in this diamagnetic complex the presence of charge-transfer bands indicate nickel-iodide bonding, but the iodide ion probably could not get close enough to the metal to coordinate if the ligands were chelated. The observation of bridging dtco ligands in this complex also helps to justify the prediction of bridging dtco ligands in $Ni_2(dtco)_3Br_4$.[5]

The chair-boat form of dtco found in $Ni(dtco)_2Cl_2$ is probably very similar to the form it takes in complexes in which it acts as a chelating agent. Only a slight increase in the S-S intraligand distance (3.335 Å) is required to achieve chelation: the smallest S-S distance in the NiS_4 plane is 3.48 Å (Figure 3).

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Registry No. $Ni(dtco)_2Cl_2$, 36006-24-3.

Supplementary Material Available. Table IV, a listing of the observed and calculated structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2079.

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Crystal and Molecular Structure of Δ-[$PtCl\{o\text{-}(C_6H_5)_2PC_6H_4C{=}CHC_6H_4P(C_6H_5)_2\text{-}o\}$]

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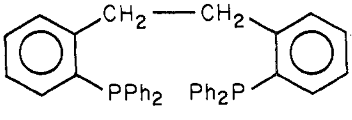
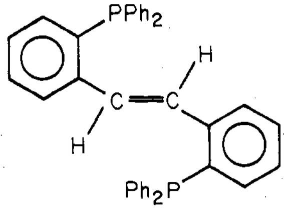
The crystal and molecular structure of Δ-{*trans*-1,2-bis[*o*-(diphenylphosphino)phenyl]ethenyl}chloroplatinum(II), Δ-[$PtCl\{o\text{-}(C_6H_5)_2PC_6H_4C{=}CHC_6H_4P(C_6H_5)_2\text{-}o\}$], has been determined by three-dimensional X-ray structural analysis using data collected by counter methods. The complex crystallizes in the acentric monoclinic space group $P2_1$ ($C_2^{\ 2}$, No. 4), with $a = 10.633$ (4) Å, $b = 16.934$ (6) Å, $c = 9.957$ (4) Å, $\beta = 119.02$ (2)°, $Z = 2$, $\rho_{obsd} = 1.64$ (1) g cm^{-3}, and $\rho_{calcd} = 1.65$ g cm^{-3}. The structure was solved by conventional Patterson and Fourier techniques and was refined by block-diagonal least-squares methods to final weighted and unweighted R factors of 0.040 and 0.042, respectively, for the 4872 unique reflections ($hk{\pm}l$ and $h\bar{k}{\pm}l$) with $I/\sigma(I) \geqslant 3.0$. The coordination at the central platinum atom is essentially square planar. The two phosphorus atoms of the novel tridentate ligand $o\text{-}(C_6H_5)_2PC_6H_4C{=}CHC_6H_4P(C_6H_5)_2\text{-}o$, are trans, and the Pt-P distances [2.266 (3) and 2.269 (3) Å] are equal within experimental error (3.0σ). The chlorine atom [Pt-Cl = 2.377 (2) Å] is trans to the σ-bonded carbon atom [Pt-C = 2.016 (8) Å], and as expected, there is a marked structural trans effect. The olefinic carbon-carbon distance is 1.336 (12) Å.

Introduction

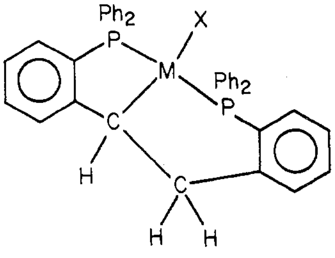
The ligand 2,2'-bis(diphenylphosphino)bibenzyl (I) loses two benzylic hydrogen atoms on reaction with rhodium(I)-chloro complexes or rhodium(III) chloride, to give chlororhodium(I) complexes of the corresponding trans stilbene ligand $o\text{-}(C_6H_5)_2PC_6H_4CH{=}CHC_6H_4P(C_6H_5)_2\text{-}o$ (II).[1] In



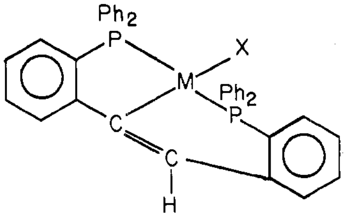
I



II



III



IV

contrast, with platinum(II) and palladium(II) complexes [*e.g.*, $MCl_2(C_6H_5CN)_2$, K_2MBr_4 (M = Pt, Pd); $PdI_2\{P(C_6H_5)_3\}_2$; PtI_2(1,5-cyclooctadiene)], reaction of I proceeds with the loss of 1 equiv of hydrogen halide and results in the formation of planar σ-bonded complexes, which, on the basis of ^{1}H and ^{31}P nmr data, have been assigned structure III.[2]

Under similar conditions, the stilbene ligand II [and its di-*o*-tolylphosphino analog $o\text{-}\{(CH_3)C_6H_4\}_2PC_6H_4CH{=}CHC_6H_4P\{(CH_3)C_6H_4\}_2\text{-}o$]^3 reacts with salts of Ni(II), Pd(II), and Pt(II), to eliminate 1 equiv of hydrogen halide and to form air-stable planar σ-bonded metal–stilbene adducts (IV).

The structure of the platinum complex IV $[PtCl\{o\text{-}(C_6H_5)_2PC_6H_4C{=}CHC_6H_4P(C_6H_5)_2\text{-}o\}]$ has been fully characterized by a single-crystal X-ray diffraction study and is now described in detail; a preliminary account of this work has appeared elsewhere.[2]

Experimental Section

Crystals of $[PtCl\{o\text{-}(C_6H_5)_2PC_6H_4C{=}CHC_6H_4P(C_6H_5)_2\text{-}o\}]$ of suitable size and quality for X-ray structural analysis were kindly supplied by Dr. M. A. Bennett and Dr. P. W. Clark of this school. *Anal.* Calcd for $C_{38}H_{29}ClP_2Pt$: C, 58.7; H, 3.8; Cl, 4.6; P, 8.0. Found: C, 58.0; H, 4.4; Cl, 4.5; P, 7.4.[4]

Crystal Data. Crystals are monoclinic, of space group $P2_1$, with $a = 10.633$ (4) Å, $b = 16.934$ (6) Å, $c = 9.957$ (4) Å, $\beta = 119.02$ (2)°, cell volume 1567.7 Å^3, $\rho_{obsd} = 1.64$ (1) g cm^{-3}, $\rho_{calcd} = 1.65$ g cm^{-3}, and $Z = 2$.

Crystals were mounted on quartz fibers with Araldite. Preliminary Weissenberg ($0kl$, $1kl$ data) and precession ($h0l$, $h1l$, $hk0$, $hk1$ data) photographs showed systematic absences ($0k0$ data for $k = 2n + 1$) corresponding to the space groups $P2_1$ (C_2^2, No. 4) and $P2_1/m$ (C_{2h}^2, No. 11). The choice of the acentric space group $P2_1$ has been confirmed by the successful solution and refinement of the structure.

The crystal chosen for data collection, of dimensions 0.015 × 0.012 × 0.012 cm, was transferred to a Picker FACS-I four-circle diffractometer and was aligned with the crystallographic a axis and the instrumental Φ axis approximately coincidental. The unit cell dimensions and crystal orientation matrix, together with estimated standard errors, were obtained from the least-squares refinement[5] of the measured 2θ, ω, χ, and Φ values of 12 carefully centered high-angle reflections ($2\theta \geqslant 29°$; graphite crystal monochromator; Mo Kα_1 radiation, λ 0.7093 Å; temperature 20 ± 1°C; takeoff angle 4.0°).

Data Collection. Reflection intensities of the type hkl, $h\bar{k}l$, $hk\bar{l}$, and $h\bar{k}\bar{l}$, within the range $3° \leqslant 2\theta \leqslant 60°$, were recorded using the θ–2θ scan technique. Peaks were scanned in 2θ from 1° below the Mo Kα_1 maximum to 1° above the Mo Kα_2 maximum, with a 2θ scan velocity of 2°/min. Backgrounds, which were assumed to be linear, were measured for 10 sec on either "side" of each reflection at the scan range limits. All reflection data were recorded using graphite crystal monochromated Mo Kα radiation, a temperature of 20 ± 1°; a tube takeoff angle of 4.0°, a crystal to counter distance of 28.5 cm, and a discriminator band-pass of 95%. The intensities of three "standard" reflections [indices (0,10,2), (530), and (005)] were monitored after every 40 measurements; none showed any significant variation during data collection. Including "standards," the intensities of 10,353 reflections were recorded.

Reflection intensities were corrected for Lorentz and polarization effects,[6] and each reflection was assigned an estimate standard deviation of the form

$$\sigma(F_o) = \{[\sigma(I)/Lp]^2 + (\rho F_o{}^2)^2\}^{1/2}/2|F_o|$$

where $\sigma(I) = [CT + (t_p/t_b)^2(B_1 + B_2)]^{1/2}$, Lp is the Lorentz–polarization factor, CT is the integrated peak intensity counted for t_p sec, B_1 and B_2 are the individual background counts counted for $t_b/2$ sec each, and ρ (=$0.002^{1/2}$) is the instrumental "uncertainty factor."[7,8] Reflections for which the individual background measurements differed significantly [*i.e.*, if $|B_1 - B_2|/(B_1 + B_2)^{1/2} \geqslant 4.0$] were discarded. The reflection data were sorted, equivalent reflection forms were averaged,[9] and those reflections for which $I/\sigma(I) < 3.0$ $\{$where $I = [CT - (t_p/t_b)(B_1 + B_2)]\}$ were discarded as being unobserved. The statistical R factor for the 4872 reflections of the terminal data set is 0.041 [$R_s = \Sigma\sigma_s(F_o)/\Sigma|F_o|$, where $\sigma_s(F_o) = \sigma(I)/2F_o(Lp)$].

Solution and Refinement of the Structure. A three-dimensional Patterson map showed the positions of the platinum atom and the two phosphorus atoms. The remaining atoms of the molecule were located from successive difference Fourier syntheses. Four cycles of block-diagonal least-squares refinement in which the overall scale factor, individual isotropic temperature factors, and atomic positional parameters for all nonhydrogen atoms were varied converged with $R = 0.104$ and $R_w = 0.109$.[10] Individual weights of the form $w = 1/\sigma^2(F_o)$ were used in all cycles of least-squares refinement. Atomic scattering factors were taken from ref 11, and those for Pt, Cl, and P were corrected for the real and imaginary parts of anomalous scattering.[12,13] Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ were introduced for all nonhydrogen atoms and refinement converged after six further cycles with $R = 0.049$ and $R_w = 0.047$. Hydrogen atom scattering contributions were not included at this stage.

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(10) $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = \{\Sigma w[|F_o| - |F_c|]^2/\Sigma w|F_o|^2\}^{1/2}$, where F_o is the observed and F_c is the calculated structure factor and w is the weight. The function minimized during least-squares refinement is $\Sigma w(|F_o| - |F_c|)^2$.

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Table I. Fractional Atomic Positional and Thermal Parameters for $[PtCl\{o\text{-}(C_6H_5)_2PC_6H_4C{=}CHC_6H_4P(C_6H_5)_2\text{-}o\}]$[a]

(a) Refined Positional and Anisotropic Thermal Parameters

ATOM	X	Y	Z	BETA11	BETA22	BETA33	BETA12	BETA13	BETA23
PT	0.44573(3)	0.25	0.22096(3)	0.00757(3)	0.00431(1)	0.00822(3)	-0.00078(4)	0.00345(2)	-0.00163(4)
CL	0.22332(26)	0.19704(17)	0.02905(32)	0.00996(31)	0.00579(14)	0.01903(45)	-0.00107(17)	0.00187(32)	-0.00397(19)
P(1)	0.57811(26)	0.15295(17)	0.19417(26)	0.01130(33)	0.00535(13)	0.01046(33)	0.00081(17)	0.00619(28)	0.00018(16)
P(2)	0.33792(25)	0.35417(15)	0.26784(24)	0.00994(29)	0.00410(11)	0.00954(29)	-0.00079(14)	0.00487(25)	-0.00079(14)
C(111)	0.6432(10)	0.1800(5)	0.0624(10)	0.0137(14)	0.0041(4)	0.0127(14)	0.0006(6)	0.0071(12)	-0.0003(6)
C(112)	0.7862(13)	0.1762(8)	0.1007(12)	0.0183(19)	0.0101(8)	0.0157(18)	0.0014(10)	0.0095(16)	0.0033(10)
C(113)	0.8270(13)	0.1962(9)	-0.0081(16)	0.0170(19)	0.0114(9)	0.0276(26)	0.0025(11)	0.0150(20)	0.0034(12)
C(114)	0.7271(14)	0.2188(7)	-0.1512(14)	0.0283(24)	0.0082(8)	0.0243(22)	0.0022(10)	0.0213(21)	0.0014(9)
C(115)	0.5889(12)	0.2207(6)	-0.1892(11)	0.0234(20)	0.0062(6)	0.0162(17)	-0.0001(7)	0.0129(16)	0.0016(7)
C(116)	0.5454(12)	0.2026(6)	-0.0836(12)	0.0192(18)	0.0052(5)	0.0164(17)	0.0000(8)	0.0101(15)	-0.0001(7)
C(121)	0.4895(9)	0.0589(6)	0.1256(10)	0.0082(11)	0.0054(5)	0.0112(13)	0.0015(6)	0.0034(10)	0.0016(6)
C(122)	0.4148(12)	0.0290(6)	0.1955(12)	0.0180(18)	0.0047(5)	0.0174(18)	0.0005(7)	0.0104(16)	0.0003(7)
C(123)	0.3491(13)	-0.0435(7)	0.1499(13)	0.0181(19)	0.0060(6)	0.0213(20)	0.0011(9)	0.0102(17)	0.0012(9)
C(124)	0.3522(13)	-0.0865(6)	0.0331(13)	0.0212(21)	0.0041(5)	0.0230(22)	0.0015(8)	0.0087(18)	0.0019(8)
C(125)	0.4282(15)	-0.0571(7)	-0.0328(13)	0.0299(26)	0.0051(6)	0.0183(19)	-0.0008(10)	0.0125(20)	-0.0024(8)
C(126)	0.4950(16)	0.0148(6)	0.0115(13)	0.0221(18)	0.0060(7)	0.0138(14)	0.0021(9)	0.0121(14)	0.0002(7)
C(131)	0.7362(9)	0.1295(6)	0.3749(10)	0.0084(11)	0.0058(5)	0.0114(13)	0.0003(6)	0.0050(10)	0.0013(6)
C(132)	0.8001(10)	0.1872(6)	0.4944(11)	0.0114(13)	0.0065(6)	0.0156(16)	0.0001(7)	0.0099(12)	0.0008(7)
C(133)	0.9230(10)	0.1640(7)	0.6280(10)	0.0123(14)	0.0075(6)	0.0105(13)	-0.0026(7)	0.0058(11)	0.0001(7)
C(134)	0.9831(12)	0.0917(7)	0.6446(12)	0.0127(15)	0.0083(7)	0.0159(17)	0.0000(8)	0.0069(14)	0.0032(9)
C(135)	0.9229(11)	0.0362(7)	0.5327(12)	0.0134(15)	0.0064(6)	0.0157(16)	0.0018(7)	0.0077(14)	0.0011(8)
C(136)	0.7998(11)	0.0562(6)	0.3984(11)	0.0146(15)	0.0060(5)	0.0132(15)	0.0026(7)	0.0063(13)	0.0008(7)
C(137)	0.7520(8)	0.2667(8)	0.4842(9)	0.0087(10)	0.0115(9)	0.0091(11)	-0.0025(9)	0.0028(9)	-0.0009(9)
C(211)	0.2714(10)	0.3335(5)	0.3996(10)	0.0146(14)	0.0044(4)	0.0117(13)	-0.0015(6)	0.0083(12)	-0.0010(6)
C(212)	0.3292(11)	0.3655(6)	0.5432(11)	0.0153(15)	0.0058(5)	0.0138(15)	-0.0023(7)	0.0078(13)	-0.0012(7)
C(213)	0.2820(12)	0.3467(6)	0.6457(10)	0.0198(18)	0.0065(5)	0.0096(13)	-0.0020(8)	0.0089(13)	-0.0005(7)
C(214)	0.1742(15)	0.2947(7)	0.6021(14)	0.0293(25)	0.0074(6)	0.0244(22)	-0.0073(10)	0.0212(22)	-0.0049(9)
C(215)	0.1174(18)	0.2648(11)	0.4652(16)	0.0514(39)	0.0162(14)	0.0380(31)	-0.0235(22)	0.0376(32)	-0.0144(19)
C(216)	0.1672(17)	0.2778(10)	0.3625(15)	0.0390(32)	0.0172(17)	0.0285(26)	-0.0205(20)	0.0245(27)	-0.0134(16)
C(221)	0.1949(9)	0.4063(5)	0.1101(10)	0.0100(12)	0.0044(4)	0.0122(13)	-0.0007(6)	0.0063(11)	-0.0014(6)
C(222)	0.1060(12)	0.4568(7)	0.1335(11)	0.0140(15)	0.0084(7)	0.0130(16)	0.0021(9)	0.0045(13)	-0.0023(8)
C(223)	0.0091(17)	0.5027(10)	0.0203(14)	0.0150(15)	0.0100(7)	0.0135(17)	0.0044(8)	0.0020(13)	-0.0027(8)
C(224)	-0.0037(13)	0.4976(8)	-0.1269(13)	0.0149(18)	0.0082(7)	0.0175(20)	0.0022(9)	0.0020(15)	0.0023(9)
C(225)	0.0804(12)	0.4460(8)	-0.1526(12)	0.0157(17)	0.0085(7)	0.0111(14)	0.0003(9)	0.0050(13)	0.0016(8)
C(226)	0.1810(10)	0.4005(6)	-0.0342(10)	0.0129(14)	0.0054(5)	0.0127(14)	0.0005(7)	0.0068(12)	0.0003(6)
C(231)	0.4843(9)	0.4262(5)	0.3590(9)	0.0092(11)	0.0045(4)	0.0075(11)	-0.0003(5)	0.0034(9)	0.0003(5)
C(232)	0.6165(10)	0.3898(6)	0.4026(10)	0.0107(12)	0.0051(5)	0.0126(14)	-0.0016(6)	0.0051(11)	-0.0002(6)
C(233)	0.7342(12)	0.4405(7)	0.4593(12)	0.0163(17)	0.0055(5)	0.0173(18)	-0.0027(8)	0.0049(15)	0.0015(8)
C(234)	0.7181(13)	0.5181(7)	0.4705(11)	0.0171(18)	0.0078(7)	0.0121(15)	-0.0054(9)	0.0036(14)	0.0009(8)
C(235)	0.5871(14)	0.5530(6)	0.4332(11)	0.0232(21)	0.0043(5)	0.0137(16)	-0.0016(8)	0.0076(15)	0.0006(7)
C(236)	0.4667(12)	0.5046(6)	0.3731(11)	0.0164(16)	0.0046(5)	0.0134(15)	-0.0019(7)	0.0065(13)	0.0001(6)
C(237)	0.6274(9)	0.3002(6)	0.3845(9)	0.0102(12)	0.0076(5)	0.0087(12)	-0.0026(7)	0.0058(10)	-0.0002(6)

(b) Calculated Hydrogen Atom Coordinates and Isotropic Thermal Parameters[b]

ATOM	X	Y	Z	B(A**2)	ATOM	X	Y	Z	B(A**2)
H(112)	0.855	0.163	0.202	8.1	H(212)	0.406	0.402	0.571	5.8
H(113)	0.926	0.194	0.018	9.4	H(213)	0.322	0.371	0.744	6.1
H(114)	0.756	0.232	-0.225	8.5	H(214)	0.141	0.281	0.672	6.3
H(115)	0.520	0.236	-0.291	6.9	H(215)	0.041	0.228	0.437	15.2
H(116)	0.447	0.205	-0.110	6.2	H(216)	0.127	0.254	0.264	14.1
H(122)	0.410	0.059	0.274	5.9	H(222)	0.118	0.461	0.233	7.1
H(123)	0.298	-0.064	0.198	7.1	H(223)	-0.050	0.538	0.039	8.3
H(124)	0.305	-0.135	0.001	7.3	H(224)	-0.072	0.529	-0.209	8.2
H(125)	0.433	-0.087	-0.111	7.9	H(225)	0.071	0.442	-0.252	7.0
H(126)	0.546	0.035	-0.037	6.4	H(226)	0.240	0.365	-0.053	5.2
H(133)	0.966	0.202	0.708	5.8	H(233)	0.826	0.419	0.489	6.8
H(134)	1.068	0.079	0.737	6.9	H(234)	0.801	0.551	0.510	7.3
H(135)	0.964	-0.015	0.546	6.0	H(235)	0.577	0.608	0.444	6.5
H(136)	0.757	0.018	0.318	5.9	H(236)	0.375	0.527	0.343	5.6

[a] Estimated standard deviations (in parentheses) in this and the following tables, and also in the text, refer to the last significant digit(s) in each case. [b] The hydrogen atoms are numbered according to the carbon atoms to which they are bonded.

Data were corrected for absorption effects using a grid of 8 × 8 × 8 points parallel to *a*, *b*, and *c**. Reflection data were re-sorted and averaged (*vide supra*), and after six further cycles, refinement converged with $R = 0.046$ and $R_w = 0.045$.

A difference Fourier synthesis at this stage showed the phenyl hydrogen atoms in stereochemically reasonable positions. Unfortunately, the peaks were rather diffuse, and accurate map coordinates could not be obtained. Consequently, calculated phenyl hydrogen atom coordinates were included, as fixed contributions to F_c, in all subsequent cycles of least-squares refinement. Hydrogen atom coordinates (assuming C–H = 0.95 Å)[14] and fixed isotropic temperature factors ($B_H = 1.1B_C$ Å^2) were recalculated after each refinement cycle. Hydrogen atom scattering factors were taken from the compilation of Stewart, *et al.*[15] Refinement converged after eight further cycles with $R = 0.042$ and $R_w = 0.040$. No attempt was made to include the hydrogen atom bonded to C(137).

On the final cycle of least-squares refinement, no individual parameter shift was greater than 0.1 esd (estimated standard deviations derive from inversion of the block-diagonal matrices). A final difference map showed no positive maxima greater than 1.2 e/Å^3, less than one-fourth of the value of typical carbon atom peaks on earlier difference maps. The standard deviation of an observation of unit weight, defined as $[\Sigma w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ [where *m* is the number of observations, and *n* (=378) is the number of parameters

(14) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).

(15) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

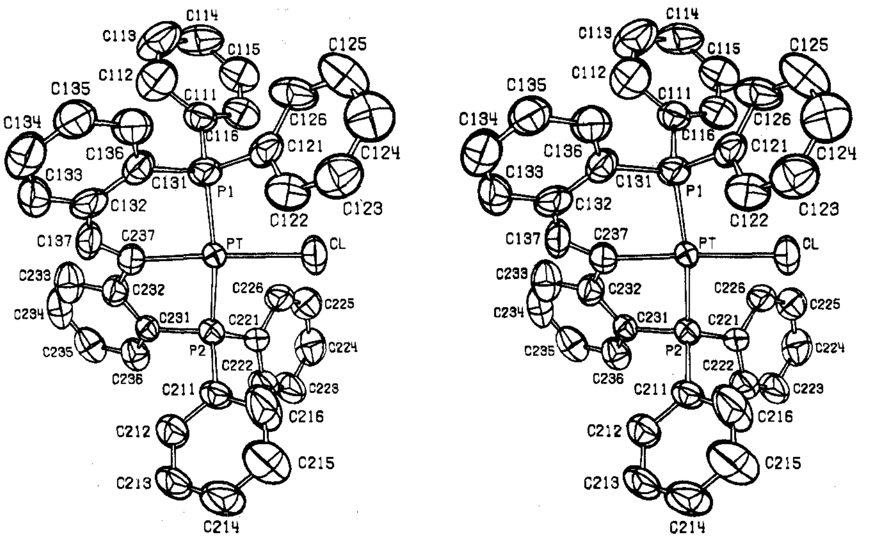

Figure 1. One molecule of [PtCl{o-(C$_6$H$_5$)$_2$PC$_6$H$_4$C=CHC$_6$H$_4$P(C$_6$H$_5$)$_2$-o}] showing the overall stereochemistry and atom numbering scheme.

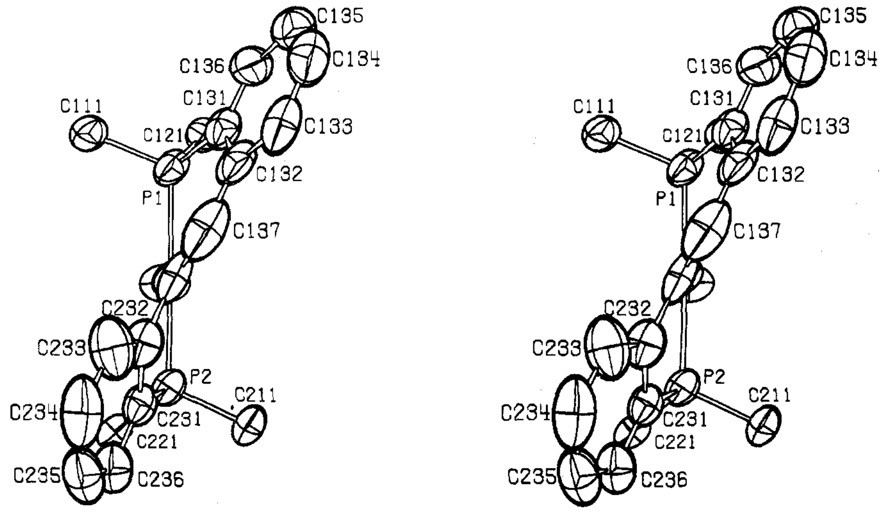

Figure 2. Principal features of the molecule as viewed along the C(237)–Pt axis showing the absolute configuration.

varied], is 1.07; *cf.* an expected value of 1.0 for ideal weighting. Comparison of the final $|F_o|$ and $|F_c|$ values shows no serious extinction effects, and there is no serious dependence of the minimized function on either $|F_o|$ or λ^{-1} sin θ. The final atomic positional and thermal parameters, together with their estimated standard deviations, where appropriate, are listed in Table I. A listing of observed and calculated structure factor amplitudes [×10 (electrons)] is available. (For details regarding the availability of supplementary material, see paragraph at end of paper.)

For the structure of inverse absolute configuration, the refinement converged with $R = 0.065$ and $R_w = 0.075$, while the standard deviation of an observation of unit weight was 2.02.

Computer Programs. The data reduction program SETUP2 (P. O. Whimp) and the sorting program SORTIE (B. M. Foxman, P. O. Whimp) were written locally for operation on the Univac 1108 computer. The Fourier program, ANUFOR, and the block-diagonal least-squares refinement program, BLKLSQ, have been described previously.[16] The absorption correction program ACACA,[17] was modified by Foxman to suit the geometry of the Picker diffractometer. The figures were produced using ORTEP,[18] while bond lengths and interbond angles, together with their estimated standard deviations, were calculated using ORFFE.[19] All calculations were carried out on the Univac 1108 computer of The Australian National University Computer Centre.

Description of the Structure

The crystal structure as defined by the cell parameters, symmetry operations, and atom coordinates of Table I consists of discrete monomeric units having neither crystallographic nor virtual symmetry higher than C_1. A perspective view of the molecule, together with the atom numbering scheme, is shown by the stereopairs of Figure 1. Figure 2 shows the molecule as viewed down the C(237)–Pt axis, and Figure 3 shows the molecule of inverse absolute configuration. In all figures, the thermal ellipsoids have been drawn to include 50% of the probability distribution, and for clarity, the hydrogen atoms have been omitted. The molecule is essentially square planar about the central platinum atom, with the phosphorus atoms of the novel tridentate ligand (C$_6$H$_5$)$_2$PC$_6$H$_4$C=CHC$_6$H$_4$P(C$_6$H$_5$)$_2$ occupying trans positions. The remaining sites are occupied by the chlorine atom and the σ-bonded carbon atom of the tridentate ligand.

Principal bond lengths and interbond angles, together with their estimated standard deviations, are listed in Table II, while bond distances and interbond angles within the six phenyl rings are listed in Table III. It should be noted that since atom-atom correlations have been neglected, both in

(16) G. B. Robertson and P. O. Whimp, *Inorg. Chem.,* **13,** 1047 (1974).

(17) B. J. Wuensch and C. T. Prewitt, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.,* 122, 24 (1965).

(18) C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(19) W. R. Busing, K. O. Martin, and H. A. Levy, Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

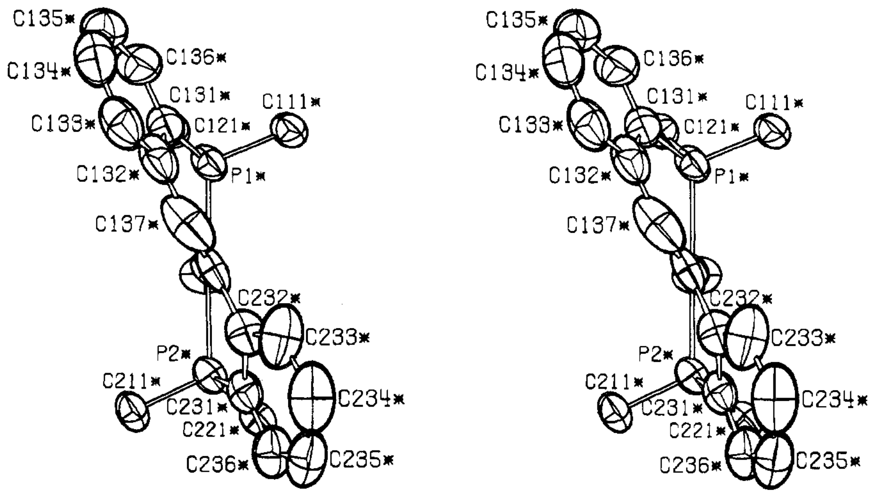

Figure 3. The molecule of inverse absolute configuration refined to an unweighted R factor of 0.065 (the starred atoms are to distinguish between this and the correct conformer).

Table II. Important Bond Lengths and Interbond Angles

(a) Bond Lengths, Å

Atoms	Distance	Atoms	Distance
Pt-Cl	2.377 (2)	Pt-P(1)	2.266 (3)
Pt-P(2)	2.269 (3)	Pt-C(237)	2.016 (8)
P(1)-C(111)	1.814 (13)	P(1)-C(121)	1.807 (10)
P(1)-C(131)	1.813 (7)	P(2)-C(211)	1.801 (13)
P(2)-C(221)	1.800 (8)	P(2)-C(231)	1.834 (9)
C(131)-C(132)	1.430 (14)	C(132)-C(137)	1.427 (18)
C(137)-C(237)	1.336 (12)	C(237)-C(232)	1.540 (15)
C(232)-C(231)	1.397 (14)		

(b) Interbond Angles, Deg

Atoms	Angle	Atoms	Angle
Cl-Pt-P(1)	93.69 (9)	Cl-Pt-P(2)	93.24 (9)
Cl-Pt-C(237)	176.8 (3)	P(1)-Pt-P(2)	173.04 (8)
P(1)-Pt-C(237)	89.5 (3)	P(2)-Pt-C(237)	83.6 (3)
Pt-P(1)-C(111)	112.4 (3)	Pt-P(1)-C(121)	116.3 (4)
Pt-P(1)-C(131)	111.9 (4)	C(111)-P(1)-C(121)	105.1 (5)
C(111)-P(1)-C(131)	106.1 (5)	C(121)-P(1)-C(131)	104.1 (4)
Pt-P(2)-C(211)	114.4 (3)	Pt-P(2)-C(221)	119.9 (4)
Pt-P(2)-C(231)	103.2 (3)	C(211)-P(2)-C(221)	105.5 (5)
C(211)-P(2)-C(231)	107.9 (4)	C(221)-P(2)-C(231)	105.1 (4)
P(1)-C(131)-C(132)	120.9 (7)	C(131)-C(132)-C(137)	125.2 (7)
C(133)-C(132)-C(137)	118.1 (9)	C(132)-C(137)-C(237)	130.2 (9)
C(137)-C(237)-C(232)	115.8 (8)	C(237)-C(232)-C(233)	123.5 (9)
C(237)-C(232)-C(231)	121.3 (8)	C(232)-C(231)-P(2)	110.2 (7)

the (block-diagonal) least-squares refinement procedure and in the subsequent calculation of bond distance and interbond angle estimated standard deviations, the tabulated esd's will certainly be underestimated. The results of weighted least-squares planes calculations are collected in Tables IV and V.[20]

Discussion

Although individual molecules of [PtCl{o-$(C_6H_5)_2PC_6H_4$-$C{=}CHC_6H_4P(C_6H_5)_2$-o}] are dissymmetric, solutions of this derivative are apparently racemic and exhibit no detectable rotation. In the solid state, the complex is resolved, and single crystals are acentric. In contrast, solutions of large single crystals are again optically inactive; while concentration effects cannot be discounted, this latter result suggests that in solution, the barrier to inversion is small, and the rate of racemization is fast. As is apparent from Figures 2 and 3, interconversion is achieved *via* rotation about the Pt-C(237) bond, with concomitant rotation about the Pt-P(1) and Pt-P(2) bonds. The absolute configuration of the isomer described in this paper is Δ.[21] A detailed discussion of the chemistry of the present complex, and related derivatives, will appear elsewhere.[4]

Despite evidence of steric strain in the molecule, particularly in the five-atom chelate ring, the platinum atom and the four coordinated ligand atoms are essentially planar. The maximum deviation from the weighted least-squares plane defined by Pt, Cl, P(1), and P(2) is 0.014 Å at P(1) ($\Delta/\sigma \approx 5$). The σ-bonded carbon atom of the tridentate o-$(C_6H_5)_2$-$PC_6H_4C{=}CHC_6H_4P(C_6H_5)_2$-$o$ ligand [C(237)] is only 0.009 (10) Å from this plane, while C(137) is 0.499 Å from the "coordination" plane.

The platinum-carbon σ-bond distance [Pt-C(237) = 2.016 (8) Å, trans to Cl] is in excellent agreement with the corresponding distance [2.03 (2) Å] in *trans*-[PtCl(CH=CH_2){P-$(CH_2CH_3)_2(C_6H_5)$}$_2$].[22] Both distances are appreciably shorter than those commonly found for simple platinum(II)-

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(20) The method used for calculating weighted least-squares planes is described by B. M. Blow, *Acta Crystallogr.*, 13, 168 (1960).

(21) IUPAC nomenclature, *Inorg. Chem.*, 9, 1 (1970).

(22) C. J. Cardin, D. J. Cardin, M. F. Lappert, and K. W. Muir, *J. Organometal. Chem.*, 60, C70 (1973).

Table III. Bond Distances and Interbond Angles within the Phenyl Rings

Atoms	$m = 1, n = 1$	$m = 1, n = 2$	$m = 1, n = 3$	$m = 2, n = 1$	$m = 2, n = 2$	$m = 2, n = 3$
			(a) Bond Distances, A			
P(*m*)-C(*mn*1)	1.814 (13)	1.807 (10)	1.813 (10)	1.801 (13)	1.800 (8)	1.834 (9)
C(*mn*1)-C(*mn*2)	1.377 (18)	1.382 (18)	1.430 (14)	1.365 (13)	1.360 (17)	1.397 (14)
C(*mn*2)-C(*mn*3)	1.381 (24)	1.377 (15)	1.395 (11)	1.375 (19)	1.353 (17)	1.392 (15)
C(*mn*3)-C(*mn*4)	1.355 (16)	1.377 (20)	1.353 (17)	1.339 (18)	1.408 (21)	1.336 (17)
C(*mn*4)-C(*mn*5)	1.328 (20)	1.354 (24)	1.358 (15)	1.297 (20)	1.360 (20)	1.389 (19)
C(*mn*5)-C(*mn*6)	1.373 (20)	1.370 (16)	1.385 (12)	1.378 (29)	1.380 (13)	1.388 (16)
C(*mn*6)-C(*mn*1)	1.369 (12)	1.385 (18)	1.378 (15)	1.363 (20)	1.374 (15)	1.358 (13)
			(b) Interbond Angles, Deg			
P(*m*)-C(*mn*1)-C(*mn*2)	123.5 (7)	117.0 (8)	120.9 (7)	123.4 (9)	121.1 (8)	110.2 (7)
P(*m*)-C(*mn*1)-C(*mn*6)	118.6 (9)	124.3 (10)	120.5 (7)	119.5 (9)	119.6 (8)	125.1 (7)
C(*mn*2)-C(*mn*1)-C(*mn*6)	117.9 (12)	118.6 (10)	118.5 (7)	116.8 (12)	119.1 (8)	124.6 (9)
C(*mn*1)-C(*mn*2)-C(*mn*3)	120.2 (9)	119.0 (12)	116.6 (9)	123.0 (10)	122.5 (13)	115.2 (9)
C(*mn*2)-C(*mn*3)-C(*mn*4)	120.2 (14)	121.6 (14)	122.6 (9)	118.4 (10)	118.3 (16)	120.9 (11)
C(*mn*3)-C(*mn*4)-C(*mn*5)	120.1 (15)	119.4 (11)	121.3 (8)	119.1 (17)	119.7 (11)	123.3 (11)
C(*mn*4)-C(*mn*5)-C(*mn*6)	120.9 (10)	119.9 (14)	118.1 (10)	124.5 (17)	120.4 (12)	117.4 (10)
C(*mn*5)-C(*mn*6)-C(*mn*1)	120.8 (11)	121.5 (15)	122.7 (9)	117.7 (13)	119.9 (11)	118.5 (11)

Table IV. Best-Weighted Least-Squares Planes

Plane	Defined by atoms	Equation[a]
1	Pt, Cl, P(1), P(2)	$0.4755X + 0.5366Y - 0.6971Z - 2.6750 = 0$
2	C(111)-C(116)	$0.0399X - 0.9563Y - 0.2896Z + 2.8162 = 0$
3	C(121)-C(126)	$-0.5694X + 0.4554Y - 0.6844Z + 2.9162 = 0$
4	C(131)-C(136)	$0.8599X + 0.3288Y - 0.3905Z - 4.6187 = 0$
5	C(211)-C(216)	$-0.5603X + 0.7421Y - 0.3678Z - 2.3639 = 0$
6	C(221)-C(226)	$-0.6519X - 0.7219Y - 0.2320Z + 6.1895 = 0$
7	C(231)-C(236)	$0.3502X + 0.1451Y - 0.9254Z + 0.6591 = 0$

[a] The equations of the planes, $LX + MY + NZ - D = 0$, refer to orthogonal coordinates where $X = 10.6332x + 0.0y - 4.8299z$, $Y = 0.0x + 16.9342y + 0.0z$, and $Z = 0.0x + 0.0y + 8.7065z$.

Table V. Deviations (A) of Atoms from Best Planes Given in Table IV

Atom	Plane 1	Atom	Plane 2	Atom	Plane 3	Atom	Plane 4	Atom	Plane 5	Atom	Plane 6	Atom	Plane 7
Pt	0.000(.3)	C(111)	0.005(9)	C(121)	0.004(10)	C(131)	0.001(10)	C(211)	0.013(10)	C(221)	-0.005(10)	C(231)	0.010(8)
Cl	0.002(3)	C(112)	-0.010(13)	C(122)	0.001(12)	C(132)	0.005(12)	C(212)	-0.002(11)	C(222)	0.007(13)	C(232)	-0.012(9)
P(1)	0.014(3)	C(113)	0.012(15)	C(123)	-0.014(13)	C(133)	-0.010(12)	C(213)	-0.008(12)	C(223)	0.004(18)	C(233)	-0.002(11)
P(2)	0.012(2)	C(114)	-0.009(12)	C(124)	0.018(13)	C(134)	0.012(13)	C(214)	0.004(14)	C(224)	-0.011(14)	C(234)	0.020(11)
C(237)	0.009(10)	C(115)	0.005(10)	C(125)	-0.011(13)	C(135)	-0.003(13)	C(215)	0.033(19)	C(225)	0.008(13)	C(235)	-0.019(11)
C(132)	-1.064(10)	C(116)	-0.006(11)	C(126)	-0.003(14)	C(136)	-0.003(12)	C(216)	-0.048(18)	C(226)	0.001(11)	C(236)	0.000(10)
C(137)	-0.499(10)	P(1)	0.058(3)	P(1)	-0.027(3)	Pt	-0.825(.3)	P(2)	-0.059(3)	P(2)	-0.181(3)	Pt	0.777(.3)
C(232)	0.617(10)					P(1)	0.052(3)					P(2)	0.177(2)
						C(137)	0.084(10)					C(237)	-0.015(9)
						C(237)	-0.115(11)					C(137)	-0.605(8)
						C(232)	0.147(11)					C(132)	-0.721(10)

alkyl complexes, *e.g.*, 2.081 (6) Å in *trans*-[PtCl(CH_3){P(CH_3)(C_6H_5)$_2$}$_2$],[23] 2.08 (1) Å in *trans*-[PtCl{$CH_2Si(CH_3)_3$}{P(CH_3)$_2$(C_6H_5)}$_2$],[24] and 2.120 (7) Å in *trans*-[PtI(CH_3){P(C_6H_5)$_3$}$_2$$SO_2$].[25] Short Pt^{II}-C σ-bond distances are also observed for *trans*-[PtCl(CF_2CH_3){P(CH_3)(C_6H_5)$_2$}$_2$] [2.014 (11) Å][23] and *trans*-[PtCl(C≡CC_6H_5){P(CH_2CH_3)$_2$(C_6H_5)}$_2$] [1.98 (2) Å].[22] The contraction of the Pt-C(CF_2CF_3) distance (*cf.* the Pt-CH_3 and Pt-$CH_2Si(CH_3)_3$ distances) has been discussed in detail elsewhere.[23] In the present complex, as in the σ-bonded vinyl and acetylide complexes,[22] the contraction of the Pt-C σ-bond distance can be attributed, in part, to the differing σ-orbital radius of carbon atoms in sp^3, sp^2, and sp hybridized states (0.77, 0.74, and 0.70 Å, respectively). In each case, however, the contraction appears to be about 0.03 Å more than can be accounted for by variations in the carbon atom σ-bond radius. In addition, in the present complex, there is a contraction of similar magnitude (0.03 Å) in each of the remaining platinum-ligand distances indicating a global contraction in the effective σ-orbital radius of the metal ion. Thus, the Pt-P distances in the present complex [Pt-P(1) = 2.266 (3) Å; Pt-P(2) = 2.269 (3) Å] are significantly shorter than the Pt-P distances in *trans*-[PtCl(CH_3){P(CH_3)(C_6H_5)$_2$}$_2$] (average 2.291 Å). Likewise, the Pt-Cl distance in the present derivative [2.377 (2) Å] is significantly shorter than the Pt-Cl distance [2.398 (4) Å] found for *trans*-[PtCl(CH=CH_2){P(CH_2CH_3)$_2$(C_6H_5)}$_2$].[22] Although this effective metal orbital contraction is most probably a consequence of conjugation and concomitant high effective electronegativity of the near-planar unsaturated ligand system, we cannot, at present, entirely eliminate the chelate effect of the strained (*vide infra*) tridentate ligand. No comparable contraction of the effective

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(23) M. A. Bennett, K. C. Ho, G. B. Robertson, and P. O. Whimp, *J. Organometal. Chem.*, in press.

(24) M. R. Collier, C. Eaborn, B. Javanovic, M. F. Lappert, L. Manojlovic-Muir, K. W. Muir, and M. M. Truelock, *J. Chem. Soc., Chem. Commun.*, 613 (1972).

(25) M. R. Snow and J. A. Ibers, *Inorg. Chem.*, **12**, 224 (1973).

platinum(II) σ-bond radius (as a consequence of conjugation) is expected for the saturated analog [PtCl{*o*-$(C_6H_5)_2PC_6H_4CHCH_2C_6H_4P(C_6H_5)_2$-*o*}] (III). Work on this derivative is in progress, but results are not yet to hand.

As expected, there is a marked structural trans effect in the present complex.[26] The Pt-Cl distance [2.377 (2) Å] is very much longer than the Pt-Cl distance of 2.294 (4) Å found for *trans*-[$PtCl_2\{P(CH_2CH_3)_3\}_2$].[27] Indeed, making allowance for the platinum atom σ-orbital contraction (0.03 Å) in the present complex, the corrected Pt-Cl distance (*ca.* 2.40 Å) is in good agreement with the value observed for the vinyl adduct *trans*-[$PtCl(CH{=}CH_2)\{P(CH_2CH_3)_2(C_6H_5)\}_2$].[22] It is interesting to note that nmr coupling constant data for the appropriate complexes have been interpreted in terms of an nmr trans effect, for σ-bonded carbon atoms, in the order $C(sp^3) \simeq C(sp^2) > C(sp)$,[26] while structural data for the complexes *trans*-[$PtCl(CH{=}CH_2)\{P(CH_2CH_3)_2(C_6H_5)\}_2$] and *trans*-[$PtCl(C{\equiv}CC_6H_5)\{P(CH_2CH_3)_2(C_6H_5)\}_2$] suggest that the ligands $-CH{=}CH_2$ and $-C{\equiv}CC_6H_5$ exert similar structural trans effects, which are only slightly less than that shown by simple alkyl groups.[22] Clearly, the present "corrected" Pt-Cl distance further supports the suggestion by Cardin, *et al.*,[22] that the trans influence of σ-bonded carbon atoms is relatively insensitive to the hybridization state of the ligating carbon atom.

The olefin distance [C(137)-C(237), 1.336 (12) Å] is within experimental error of the value normally expected for a simple carbon-carbon double bond [1.335 (5) Å].[28] The distance Pt-C(137) [3.048 (7) Å] indicates that there is little, if any, interaction between the platinum atom and this carbon atom. The distance C(132)-C(137) [1.427 (18) Å] is within experimental error of its expected value [*ca.* 1.48 Å], although the observed value is certainly consistent with conjugation of the ligand. In contrast, C(232)-C(237) [1.540 (15) Å] is significantly longer and probably reflects the steric strain in the five-atom chelate ring (*vide infra*).

Five of the P-C distances range from 1.800 (8) to 1.814 (13) Å (average 1.807 Å) and are only slightly shorter than the average P-C distance of 1.828 Å found for free triphenylphosphine.[29] The distance P(2)-C(231) [1.834 (9) Å] is marginally longer than the mean value ($\Delta/\sigma \simeq 2.5$) possibly as a consequence of fairly severe steric strain in the five-atom chelate ring. In particular, the severe deformation of the angle Pt-P(2)-C(231) [103.2 (3)°] by *ca.* 13° from its expected value of *ca.* 116°[30] clearly implies a substantial modification of the phosphorus atom σ-bonding orbital mixing coefficients. Additional evidence of strain in the five-atom chelate ring is provided by the angles P(2)-Pt-C(237) [83.6 (3)°], P(2)-C(231)-C(232) [110.2 (7)°], and Pt-C(237)-C(232) [114.4 (5)°] which deviate significantly from their expected values of 90, 120, and 120°, respectively. As expected, the six-atom chelate ring appears to be less strained although there are angular distortions at C(137) and C(237) [*i.e.*, Pt-C(237)-C(137) = 129.7 (9)°; C(132)-C(137)-C(237) = 130.2 (9)°; *cf.* expected values of 120°]. However, within this six-atom chelate ring, the angles at Pt, P(1), and C(131) are within experimental error of their accepted values. The C-P-C angles in the present complex average 105.6° and, as expected for both free and coordinated triphenylphosphine, are all less than the tetrahedral angle. Within the six phenyl rings, the carbon-carbon distances average 1.371 Å, while the C-C-C angles average 120.0°.

There are no unusually short intermolecular atom-atom contacts.

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Registry No. [PtCl{*o*-$(C_6H_5)_2PC_6H_4C{=}CHC_6H_4P(C_6H_5)_2$-*o*}], 51705-83-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $4.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2082.

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